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(57) Abstract

A new range of epoxides having at least one primary epoxide group is provided. The epoxides are obtained from esterification products having at least one primary alkenyl group, which esterification products are yielded when an alcohol is esterified, at a molar ratio hydroxyl to carboxyl groups of 1:0.8 to 1:5, with at least one linear or branched alkenoic acid having one carboxyl group and one primary alkenyl group. The alkenyl group or groups in said esterification products is/are, after an optional removal of excess or otherwise unreacted carboxylic acid, oxidized in the presence of an effective amount of at least one oxidizing agent to yield corresponding number of primary epoxide groups. In a further aspect, a process for production of said epoxides is provided and in yet a further aspect a curable composition comprising at least one epoxide as provided by the present invention.

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NOVEL PRIMARY EPOXIDES

The present invention provides a new range of epoxides having at least one primary epoxide group, which epoxides are obtained from esterification products having at least one primary alkenyl group, which esterification products are yielded when an alcohol is esterified with an alkenoic acid having said primary alkenyl group. The alkenyl group or groups in said esterification products is/are oxidized in the presence of an oxidizing agent to yield said primary epoxide group or groups. In a further aspect, the present invention refers to a process for production of said epoxide and in yet a further aspect to a curable composition comprising said epoxide.

Epoxy resins and other epoxides are well-known and have been manufactured for a very long time. Epoxides include compounds obtained from epihalohydrins by its reaction with hydroxyl or carboxyl containing compounds, such as phenols, alcohols, carboxylic acids and hydroxy or carboxyfunctional esters, polyesters, ethers or polyethers, yielding epoxides having primary epoxide groups. The by far most commonly used epihalohydrin is epichlorohydrin yielding glycidyl ethers and esters. Phenols, alcohols and hydroxyfunctional esters or polyesters are of particular merit. A further class of epoxides can be exemplified by compounds obtained by oxidation (epoxidation) of oxidizable olefinic double bonds, such as oxidation of unsaturated carboxylic acids and unsaturated esters, polyesters, ethers or polyethers. Numerous procedures are available for carrying out said oxidation, but the most widely used procedure is by far the direct oxidation with organic peroxy or haloperoxy acids. Compounds of particular merit are here unsaturated carboxylic acids designated as fatty acids and unsaturated esters or polyesters.

Ordinary epoxide functional compounds exhibit many good properties but are also submitted to some drawbacks related to for instance rheological properties and ratio between viscosity and molecular weight. A conventional epoxide functional compound normally exhibits a very high viscosity in relation to its molecular weight and often requires a certain amount of diluents, preferably reactive diluents. Said diluents are often mono or difunctional low molecular compounds such as glycidyl ethers and compounds produced from unsaturated fatty acids or unsaturated fatty acid esters. Substantial drawbacks are for instance that low molecular epoxide compounds such as said glycidyl ethers are more or less toxic and that known and available epoxides produced from unsaturated fatty acids or unsaturated fatty acid esters are compounds having secondary epoxide groups. The reactivity enthalpy decreases with secondary epoxide groups, which also may

negatively influence the curing thus leaving residual unreacted epoxide groups in a cured material.

Various epoxides, their properties and various epoxidation procedures are thoroughly disclosed and discussed in available literature on chemical as well as polymer science and technology, such as Kirk-Othmer, "*Encyclopedia of Chemical Technology*" - Wiley-Interscience Publication, 1980. vol. 9, pp. 251-290 "Epoxidation" and pp. 267-290 "Epoxy Resins" and *Handbook of Epoxy Resins*, by Henry Lee and Kris Neville, 1982 reissue, McGraw-Hill Book Company, New York. Further disclosures can be found in for instance "*Encyclopedia of Polymer Science and Technology*" - John Wiley & Sons, Inc. 1967, vol. 6 pp. 83-270 "Epoxidation", pp. 196-209 "1,2-Epoxide Polymers" and pp. 209-271 "Epoxy Resins".

It is an object of the present invention to provide epoxides, having at least one primary epoxide group, wherein a high reactivity and a high molecular weight are combined with a low viscosity in relation to said molecular weight, wherein said properties are obtained without employing epihalohydrins as oxidizing agents and wherein the drawbacks disclosed above are substantially eliminated or reduced. According to the present invention, epoxides are produced from esterification products having at least one primary alkenyl group, which esterification products are yielded when an alcohol is esterified at a molar ratio hydroxyl to carboxyl groups of 1:0.8 to 1:2 with at least one linear or branched alkenoic acid having said primary alkenyl group. The alkenyl group or groups in said esterification products is/are, after an optional removal of excess of said alkenoic acid, subjected to oxidation (epoxidation) in the presence of an effective amount of at least one oxidizing agent to yield said primary epoxide group or groups. The present invention accordingly provides a new range of epoxides having one or more primary epoxide groups. These epoxides exhibit excellent reactivity and curing properties as well as viscosities providing good to excellent diluting properties despite a relatively high molecular weight. An epoxide according to the present invention can, furthermore, as being a substantially aliphatic compound not being a glycidyl ether and having a comparatively high molecular weight, be expected to exhibit comparatively low toxicity. This assumption finds support in "*Epoxy Resins and Curing Agents*" - "Toxicology, health, safety and environmental aspects" prepared by APME's Epoxy Resins Committee and published January 1996. This publication gives at hand that epoxides having a molecular weight of more than 700 not are readily bioavailable and exhibits an acute toxicity which is likely to be very low and that reactive diluents having a

molecular weights of less than 700 are likely to be irritants and/or sensitizers presenting a higher toxicity risk. Epoxides provided by the present invention are products having relatively high molecular weights yet being low viscous enough to provide excellent diluting properties. The epoxides are advantageously used in application areas such as epoxide functional reactive diluents and flexibilizers and epoxyacrylate precursors. It has furthermore been found that the epoxides of the present invention readily cure with epoxy curing agents at room temperature. This is contrary to what is generally found in handbooks and similar publication. It can for instance in "*Handbook of Epoxy Resins*", by Henry Lee and Kris Neville, 1982 reissue, McGraw-Hill Book Company, New York, be read regarding polyfunctional flexibilizers "Glycidyl resins are capable of providing flexibilizing properties not conveniently obtainable with lower-cost molecules. Non-glycidyl-type resins would not, in the main, appear of equal value, insofar as such resins are generally unreactive with epoxy curing agents at room temperature.", page 16-3.

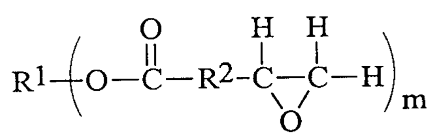
An epoxide of the present invention is as previously disclosed obtained from an esterification product yielded when esterifying an alcohol and at least one alkenoic acid. The alcohol is in preferred embodiments of the present invention selected from di, tri and polyalcohols optionally having one or more ester and/or ether groups, such as 2-alkyl-1,3-propanediols, 2,2-dialkyl-1,3-propanediols, 2-hydroxyalkyl-1,3-propanediols, 2-alkyl-2-hydroxyalkyl-1,3-propanediols, 2,2-di(hydroxyalkyl)-1,3-propanediols, 1,2,3-propanetriols and dimers, trimers or polymers thereof. These alcohols can suitably be exemplified by neopentyl glycol, 2-ethyl-2-butyl-1,3-propanediol, trimethylolethane, trimethylolpropane, pentaerythritol, glycerol, di and trimers of neopentyl glycol, ditrimethylolethane, ditrimethylolpropane, dipentaerythritol, diglycerol and tritrimethylolpropane. The alcohol can, furthermore, suitably and advantageously be selected from condensation products between di, tri or polyalcohols and at least one alkylene oxide, such as ethylene oxide, propylene oxide, butylene oxide and/or phenylethylene oxide. Alcohols having a neopentyl structure are especially preferred as these compounds normally provide improved chemical as well as thermal stability. Said at least one alkenoic acid is, in likewise preferred embodiments of the present invention, an alkenoic acid having 3-24, preferably 6-18 or 8-12, carbon atoms in its primary chain, such as Δ9,10-decenoic acid, Δ10,11-undecenoic acid or mixtures thereof.

An epoxide is, in the most preferred embodiments of the present invention, obtained by oxidation of the alkenyl group or groups in an esterification product

yielded when trimethylolpropane or alkoxylated, such as ethoxylated or propoxylated, trimethylolpropane is esterified with Δ10,11-undecenoic acid at said molar ratio.

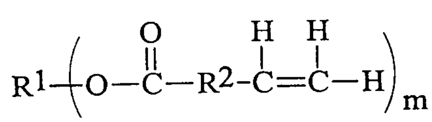
Suitable oxidizing agents for oxidation (epoxidation) of said primary alkenyl group or groups are to be found among for instance peroxy and haloperoxy acids. Peroxy and haloperoxy acids can be exemplified by peroxyformic acid, peroxyacetic acid, peroxybenzoic acid, *m*-chloroperoxybenzoic acid, trifluoroperoxyacetic acid and mixtures thereof or therewith. Said oxidizing agent can either be pre-produced or produced *in situ*, that is during and/or pendant to said oxidation, from for instance peroxides and carboxylic acids, such as from hydrogen peroxide and formic acid or acetic acid, preferably in the presence of a catalysing agent, such as a sulphonic acid and/or an ion exchange resin.

The epoxides of the present invention can suitably be further explained by for instance the general formula (I) wherein R^1 is linear or branched alkanyl or hydroxyalkanyl and wherein R^2 is linear or branched alkanyl or alkenyl and m is an integer and at least 1.



Formula (I)

Formula (I) is derived from an ester of general formula (II) wherein the alkenyl group has been oxidized (epoxidized) to yield an epoxide group. R^1, R^2 and m in formula (II) are as previously disclosed.



Formula (II)

Formula (II) is derived from an alcohol of general formula (III) which has been esterified with an alkenoic acid of general formula (IV) at a molar ratio hydroxyl to carboxyl groups of 1:0.8 to 1:5, such as 1:2 or 1:1. The optional excess of carboxylic acid, that is a molar ratio hydroxyl to carboxyl groups of 1:>1, or during the esterification unesterified carboxylic acid is optionally removed before oxidation (epoxidation). R^1 and R^2 in formula (III) and (IV) are as previously disclosed and n is an integer and at least 1, preferably an integer between 2-8.

Formula (III) Formula (IV)

$$R^1\text{-}(OH)_n$$

$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-R^2-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H$$

The mean value $\bar{m}$ for m in formula (I) and (II) is in preferred embodiments, wherein n is an integer between 2-8, a value between 0.8 x n and n, optional excess of carboxylic acid or during the esterification unreacted carboxylic acid is not counted. Preferred embodiments of the epoxides of the present invention can accordingly be disclosed by general formula (I) wherein R^1 and R^2 are as previously disclosed and wherein the mean value $\bar{m}$ for m is between 1.6 and 8.

In a further aspect, the present invention refers to a process in two or more steps for production of an epoxide as previously disclosed. The process comprises the steps of

i) esterifying, in a first step, an alcohol with at least one linear or branched alkenoic acid, which acid has one carboxyl group and one primary alkenyl group, at a molar ratio hydroxyl to carboxyl groups of 1:0.8 to 1:2, whereby an ester having at least one primary alkenyl group is yielded, and
ii) oxidizing, in a subsequent step, the primary alkenyl group or groups in yielded ester in the presence of an effective amount of at least one oxidizing agent, whereby an epoxide having at least one primary epoxide group is yielded.

The alcohol is in preferred embodiments esterified with said at least one alkenoic acid at a temperature of 120-280°C and excess or otherwise unreacted alkenoic acid is optionally removed before oxidation of the alkenyl group or groups.

Preferred alcohols and preferred alkenoic acids are as previously disclosed for the primary epoxide of the present invention.

Oxidizing agents are in preferred embodiments as previously disclosed peroxy and haloperoxy acids, such as peroxyformic acid, peroxyacetic acid, peroxybenzoic acid, *m*-chloroperoxybenzoic acid, trifluoroperoxyacetic acid or mixtures thereof or therewith. Peroxy and haloperoxy acids can as also previous disclosed be pre-produced or produced *in situ* from a peroxide and a carboxylic acid, such as from hydrogen peroxide and formic acid and/or acetic acid, preferably in the presence of a catalyzing agent, such as a sulphonic acid, for example

methanesulphonic acid and/or *p*-toluenesulphonic acid, and/or an ion exchange resin catalyst.

Preferred embodiments of the process include the presence of at least one catalyst such as an acid catalyst, such as a Brønsted acid, a Lewis acid, an ion exchange resin, and/or a metal oxide, a metal hydroxide, an organometallic compound and/or a titanate, during the esterification, which catalyst optionally also is present during the oxidation. especially preferred catalysts are for example methanesulphonic acid, *p*-toluenesulphonic and ion exchange resins.

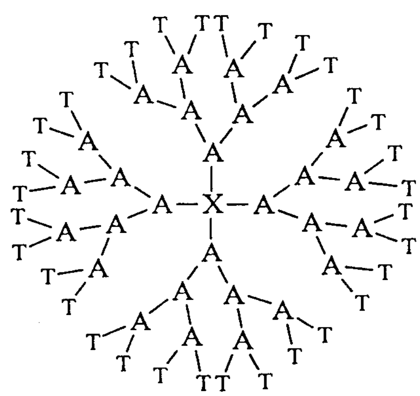
Trimethylolpropane and alkoxylated, such as ethoxylated or propoxylated, trimethylolpropane are, in the most preferred embodiment of the process, esterified with Δ10,11-undecenoic acid at a temperature of 150-240°C and at a molar ratio of hydroxyl groups to acid groups of 1:0.9 to 1:1.2. The primary alkenyl groups in yielded ester are subsequently oxidized in the presence of pre-produced or *in situ* produced peroxyformic, peroxyacetic acid and/or *m*-chloroperoxybenzoic acid.

In yet a further aspect, the present invention refers to a curable composition comprising two or more components whereby at least one component is a primary epoxide according to the present invention and as previously disclosed. The composition can also suitably, in addition to said epoxide, comprise at least one hyperbranched or dendritic macromolecule and/or a hyperbranched or dendritic dendron as defined below.

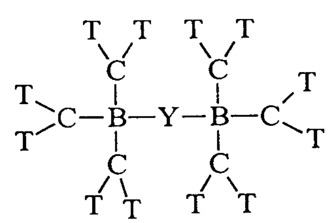
Hyperbranched and dendritic macromolecules, including dendrimers, can generally be described as three dimensional highly branched molecules having a treelike structure. Dendrimers are highly symmetric, while similar macromolecules designated as dendritic or hyperbranched may to a certain degree hold an asymmetry, yet maintaining the highly branched treelike structure. Dendrimers are monodisperse or substantially monodisperse hyperbranched or dendritic macromolecules. Hyperbranched and dendritic macromolecules normally consist of an initiator or core (nucleus) having one or more reactive sites and a number of branching layers, comprising at least one branching chain extender, and optionally one or more spacing layers, comprising at least one spacing chain extender, and/or a layer of chain terminating molecules. A spacing chain extender is here defined as a compound having two reactive groups or sites and a branching chain extender as a compound having at least three reactive groups or sites. Continued replication of branching layers normally yields increased branch multiplicity and, where

applicable or desired, increased number of terminal functions or sites. The layers are usually called generations and the branches dendrons. Terminal groups or sites in the hyperbranched or dendritic macromolecule may be functionalized, such as oxidized, allylated, acrylated etc., to yield desired terminal functions, groups or sites. Hyperbranched dendritic macromolecules can be illustrated by below simplified formula (V) and (VI) wherein X and Y are initiators or cores having four and two reactive sites, respectively, and A, B and C are branching chain extenders having three (A and C) and four (B) reactive sites, each branching chain extender forming one branching generation in the macromolecule. T is a terminating chain stopper or a suitable terminal function or site, such a hydroxyl, a carboxyl or an epoxide group. The hyperbranched dendritic macromolecule of formula (V) holds four equal and the macromolecule of Formula (VI) two equal dendritic so called dendrons linked to respective core. The dendrons, which have three branching generations, of the macromolecule of formula (V) is as disclosed by simplified Formula (VII).

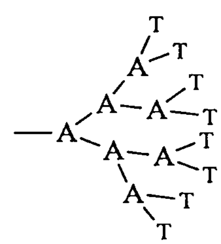
Formula (V)



Formula (VI)



Formula (VII)



A dendron can be pre-produced, and then added to a nucleus, by for instance condensing one or more hydroxyfunctional carboxylic acids, by allowing mono, di, tri or polyfunctional carboxylic acids to form esterlinks with mono, di, tri or polyfunctional alcohols or epoxides or by similar procedures resulting in esterlinks, etherlinks or other chemical bonds. The raw materials used to produce a dendron must be chosen to provide at least one terminal function reactable to the core or initiator. A dendron can of course be a hyperbranched or dendritic molecule or macromolecule per se and can of course be used in applications similar to hyperbranched and dendritic macromolecules composed of said core and said dendron or dendrons as disclosed above. A dendron is accordingly possible to functionalize, such as oxidize, allylate, acrylate, halogenate etc., to yield desired

terminal functions, groups or sites. A dendron can for instance be built up by polycondensing compounds having three or more reactive groups, such as di, tri or polyhydroxyfunctional carboxylic acids.

The preferred hyperbranched or dendritic macromolecule used in embodiments of the composition according to the present invention is built up from a core and at least one dendron comprising at least one generation built up from at least one branching chain extender. Said hyperbranched or dendritic macromolecule is preferably a macromolecule of polyester type, whereby the core is derived from a compound having at least one reactive hydroxyl or epoxide group and the chain extender is a compound having at least three reactive groups of which at least one is a carboxyl group and at least one is a hydroxyl group and whereby terminal groups in said macromolecule substantially are hydroxyl groups. The macromolecule may also optionally be chain terminated and/or further functionalized to provide desired terminal functions. The hyperbranched or dendritic macromolecule is accordingly substantially build up from ester units optionally in combination with ether, thioether, amine and/or amidoamine units. Hyperbranched and dendritic macromolecules of polyester type are thoroughly disclosed and discussed in the Swedish patents nos. 468 771 and 503 342.

A hyperbranched or dendritic dendron as included according to embodiments in the composition of the present invention comprises suitably at least one generation built up from at least one branching chain extender, whereby said branching chain extender is a compound having at least three reactive groups of which at least one is a carboxyl group and at least one is a hydroxyl group. The dendron can optionally be chain terminated, further functionalized and/or protected.

A dendron, including the dendrons of the hyperbranched or dendritic macromolecule, which macromolecule is composed of a core and chain extenders as disclosed above, can for instance be built up by polycondensing compounds having three or more reactive groups, such as di, tri or polyhydroxyfunctional carboxylic acids. Hydroxyfunctional acids can suitably be exemplified by compounds such as 2,2-dimethylolpropionic acid, α,α-bis(hydroxymethyl)butyric acid, α,α,α-tris(hydroxymethyl)acetic acid, α,α-bis(hydroxymethyl)valeric acid, α,α-bis(hydroxy)propionic acid, α,β-dihydroxypropionic acid, 3,5-dihydroxybenzoic acid, heptonic acid, citric acid and mixtures of two or more of said acids.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The

following preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever. Examples 1-7 refer to

- Example 1 and 2: Preparation of epoxides according to embodiments of the present invention.
- Example 3: Preparation of resin compositions comprising the epoxide of Example 1 and a commercial bisphenol-A diglycidyl ether.
- Example 4 and 5: Evaluation of the resin compositions of Example 3.
- Example 6: Resin compositions comprising the epoxide of Example 2, a commercial dendritic macromolecule and a commercial bisphenol-A epoxide.
- Example 7: Determination of the reaction enthalpy of a primary epoxide according to the invention compared to a secondary epoxide.

Example 1

Step 1: Esterification

5 moles of trimethylolpropane (TMP 99, Perstorp Polyols) and 15 moles of Δ10,11-undecenoic acid were together with 3% of xylene, as azeotropic solvent, charged in a 4-necked reaction flask equipped with stirrer, thermometer and water-trap (Dean-Stark). The reaction mixture was heated to 170°C and thereafter during 5 hours to 240°C. The esterification was allowed to continue at 240°C until an acid value of 10-12 mg KOH/g was obtained. Yielded ester was cooled to room temperature and analysed with below result.

Hydroxyl value, mg KOH/g	10
Acid number, mg KOH/g	11.1
Unsaturation, I_2/100g	93.7
Viscosity at 23°C, mPas	91
Non-volatile matter, %	97.3

Step 2: Oxidation

The ester yielded in Step 1 was diluted with 65% by weight of xylene and heated to 60°C followed by addition of 4% by weight of an ion exchange resin (Dowex™ M-31H, Dow Chemicals Co.), 0.5 mole/mole unsaturation of acetic acid and 1.45 mole/mole unsaturation of hydrogen peroxide. The reaction was allowed to continue for 10 hours and obtained product solution was then centrifuged at 4500 rpm for 20 minutes. The organic phase was recovered, subsequently washed 3

times with 10% by weight of water and finally evaporated in a roll evaporator and analysed with below result.

Molecular weight, g/mole	680
Epoxy equivalent weight, g/eq.	314
Remaining unsaturation, I_2/100g	21.3
Acid value, mg KOH/g	7.6
Viscosity at 23°C, mPas	176
Non-volatile matter, %	95.2
Yield, %	72.9

Obtained epoxide exhibit a very low viscosity at a molecular weight very close to the critical molecular weight of 700 g/mole as disclosed in previously discussed "*Epoxy Resins and Curing Agents*", APME's Epoxy Resins Committee 1996.

Example 2

Step 1: Esterification

5 moles of ethoxylated trimethylolpropane (Polyol TP 70™, Perstorp Polyols) and 15 moles of Δ10,11-undecenoic acid were together with 3% of xylene, as azeotropic solvent, charged in a 4-necked reaction flask equipped with stirrer, thermometer and water-trap (Dean-Stark). The reaction mixture was heated to 190°C and thereafter during 6 hours to 230°C. The esterification was allowed to continue at 240°C until an acid value of 10-12 mg KOH/g was obtained. Yielded ester was cooled to room temperature and analysed with below result.

Hydroxyl value, mg KOH/g	17
Acid number, mg KOH/g	10.8
Viscosity at 23°C, mPas	101
Non-volatile matter, %	98.1

Step 2: Oxidation

The ester yielded in Step 1 was diluted with 65% by weight of xylene and heated to 60°C followed by addition of 1.25 mole/mole unsaturation of peroxyacetic acid. The reaction was allowed to continue for 3 hours and obtained product solution was then centrifuged at 4500 rpm for 20 minutes. The organic phase was

recovered, subsequently washed 3 times with 10% by weight of water and finally evaporated in a roll evaporator and analysed with below result.

Molecular weight, g/mole	989
Epoxy equivalent weight, g/eq.	368
Acid value, mg KOH/g	12.1
Viscosity at 23°C, mPas	126
Non-volatile matter, %	91.0
Yield, %	89.5

Obtained epoxide exhibit a very low viscosity at a molecular weight substantially above the critical molecular weight of 700 g/mole as disclosed in previously discussed "*Epoxy Resins and Curing Agents*", APME's Epoxy Resins Committee 1996.

Example 3

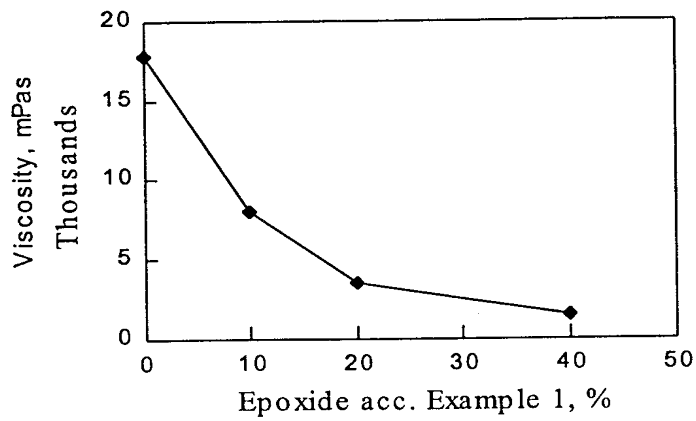
Resin compositions were prepared by mixing the epoxide according to Example 1 with a commercial bisphenol-A diglycidyl ether (Epikote® 880, Shell Chemicals) at weight percentages as given in Table 1 below and the dilution properties of the epoxide according to Example 1 was determined. The result is given in Graph 1 below. Epikote® 880, which had a viscosity at 23°C of 17800 mPas, was without admixed epoxide according to Example 1 used as control.

Table 1

	Control	Sample 1	Sample 2	Sample 3
Epoxide according to Example 1, g:	0	10	20	40
Epikote® 880, g:	100	90	80	60

The components were mixed at 23°C using mechanical stirring for 5 minutes and subsequently degassed at 23°C in a vacuum chamber at 0.1 bar for 10 minutes.

Graph 1



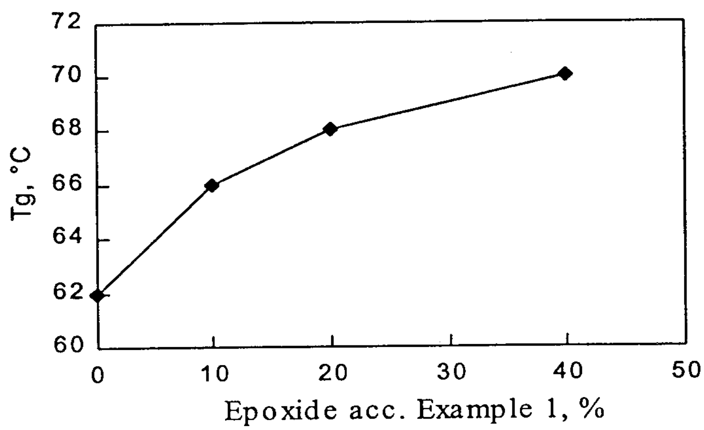
The result show that the epoxide according to the invention as obtained in Example 1 has excellent diluting properties and substantially reduces the initial viscosity exhibited by Epikote® 880, without essentially affecting the average molecular weight.

Example 4

A commercial isophorone diamine curing agent (Hardener HY 5083, Ciba-Geigy, Switzerland) was in amounts giving a molar ratio epoxide groups to amine groups of 1:1 mixed into Samples 1-3 and Control as obtained in Example 3. The components were mixed at 23°C using mechanical stirring for 5 minutes and the resin compositions were subsequently degassed at 23°C in a vacuum chamber at 0.1 bar for 10 minutes.

The resin compositions were poured into steel moulds having the internal dimensions 15 x 7 x 3 mm and cured at 23°C and 50% relative humidity for 5 days to yield specimens of said dimensions. The glass transition temperatures (Tg) were determined and are given in Graph 2 below.

Graph 2



The result show that the epoxide according to the invention as obtained in Example 1 cure at room temperature and has a substantial positive effect on the Tg value of specimens obtained from resin compositions.

Example 5

The mechanical properties of specimens obtained from Sample 3 and Control (see Example 3 and 4) were evaluated. The result is given in Table 2 below.

Table 2

	Control	Sample 3
E, GPa	--	1.1
E_{DYN}, GPa	--	3.0
K_{1c}, MPa.m^{½}	--	1.69
Flexural strength, MPa	--	87.5
Flexural strain, %	--	7.2

E = Tensile modulus
E_{DYN} = Dynamic elasticity
K_{1c} = Critical stress intensity factor

The control specimens (composition without epoxide according to Example 1) were very brittle and mechanical evaluation could not be performed. The result

clearly shows that the epoxide according to the present invention substantially improves mechanical properties. This is further enhanced by a limited evaluation of Sample 2 (se Example 3 and 4) giving a K_{1c} value of 0.64 MPa.m^{½} and an E_{DYN} value of 4.2 GPa.

Example 6

Two resin compositions (Sample 1 and 2) were prepared by mixing small amounts of the epoxide according to Example 2, as reactive diluent, with a commercially available dendritic epoxide having an EEW value of 400 g/eq, a molecular weight of 10000 and a viscosity of 20000 mPas (Boltorn® E2, Perstorp Polyols) and a commercial bisphenol-A epoxide (Araldit® LY 556, Ciba-Geigy). A commercial methyl tetrahydrophthalic anhydride hardener (HY 917, Ciba-Geigy, Switzerland) and a commercial 1-methylimidazol accelerator (DY 070, Ciba-Geigy) were subsequently admixed. A similar resin composition without epoxide according to Example 2 and without Boltorn® E2 (to determine respective contribution) was also prepared and used as control.

The resin compositions were poured into steel moulds having the internal dimensions 15 x 7 x 3 mm and cured at 23°C and 50% relative humidity for 5 days to yield specimens of said dimensions. The flexural strain was determined and is given in Table 3 below together with formulations of the resin compositions.

Table 3

	Control	Sample 1	Sample 2
Araldit® LY 556, g	100	100	100
Boltorn® E2, g	---	10	10
Epoxide acc. to Example 2 (reactive diluent), g	---	1	2
Hardener HY 917, g	90	90	90
Accelerator DY 070, g	1	1	1
Flexural strain, %	7.3	8.5	10
E_{DYN}, GPa	3.1	3.0	2.9
Flexural yield stress, MPa	137	134	135
Tg, °C	137	136	135

E_{DYN} = Dynamic elasticity
Tg = Glass transition temperature

Small amounts of the epoxide according to the invention have as can be seen substantial effect on the flexural strength without negatively effecting thermodynamic properties. The Tg value is frequently reported to decrease with increasing amount of reactive diluent, such as epoxidized glycols.

Example 7

Epoxides were prepared from (i) Δ10,11-undecenoic acid ester (primary epoxide according to the invention) and (ii) oleic acid ester (secondary epoxide - comparative sample). Esterification and oxidation were performed in accordance with Examples 1 and 2. The reaction enthalpy was determined by means of DSC according to below procedure.

DSC Procedure

Isophorone diamine and respective ester were mixed at a molar ratio amine to epoxide of 1:1 and the reaction enthalpy was determined using following parameters: 30-300°C, 10°C and 50 bar N_2. Obtained result is given in Table 4 below.

Table 4

	Sample (i)	Sample (ii)
Specific reaction entalpi, kJ/mole	38.1	9.7
Left limit, °C	88.7	148.5
Peak, °C	184	198

The result shows that the epoxide according to the invention, Sample (i), being a primary epoxide, exhibits compared to a similar secondary epoxide a substantially increased reaction enthalpy with a substantially reduced left limit, which is the point where curing starts, and reduced peak temperature.

CLAIMS

1. An epoxide having at least one primary epoxide group **characterised in**, that it is obtained from an esterification product having at least one primary alkenyl group, which esterification product is yielded when an alcohol is esterified, at a molar ratio hydroxyl to carboxyl groups of 1:0.8 to 1:5, preferably 1:0.8 to 1:2 with, at least one linear or branched alkenoic acid having one carboxyl group and one primary alkenyl group, whereby said alkenyl group in said esterification product, after an optional removal of excess or otherwise unreacted carboxylic acid, is oxidized in the presence of an effective amount of at least one oxidizing agent to yield said primary epoxide group.

2. An epoxide according to Claim 1 **characterised in**, that said alcohol is a di, tri or polyalcohol optionally having one or more ester and/or ether groups.

3. An epoxide according to Claim 2 **characterised in**, that said di, tri or polyalcohol is a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxyalkyl-1,3-propanediol, a 2-alkyl-2-hydroxyalkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 1,2,3-propanetriol or a dimer, trimer or polymer thereof.

4. An epoxide according to Claim 2 or 3 **characterised in**, that said di, tri or polyalcohol is neopentyl glycol, 2-ethyl-2-butyl-1,3-propanediol, glycerol, trimethylolethane, trimethylolpropane or pentaerythritol or a dimer, trimer or polymer thereof.

5. An epoxide according to Claim 1 **characterised in**, that said alcohol is a condensation product between a di, tri or polyalcohol and at least one alkylene oxide.

6. An epoxide according to Claim 5 **characterised in**, that said alkylene oxide is ethylene oxide, propylene oxide, butylene oxide, phenylethylene oxide or a mixture thereof.

7. An epoxide according to any of the Claims 1-6 **characterised in**, that said at least one alkenoic acid has 3-24, such as 6-18 or 8-12, carbon atoms in its primary chain.

8. An epoxide according to any of the Claims 1-7 **characterised in**, that said at least one alkenoic acid is Δ9,10-decenoic acid, Δ10,11-undecenoic acid or a mixture thereof.

9. An epoxide according to Claim 1 **characterised in**, that said alcohol is trimethylolpropane or alkoxylated, such as ethoxylated, trimethylolpropane and that said at least one alkenoic acid is Δ10,11-undecenoic acid.

10. A process in two or more steps for production of an epoxide according to Claim 1 **characterised in**, that

    i) that an alcohol in a first step is esterified with at least one linear or branched alkenoic acid, which acid has one carboxyl group and one primary alkenyl group, at a molar ratio hydroxyl to carboxyl groups of 1:0.8 to 1:2, whereby an ester having at least one primary alkenyl group is yielded, and
    ii) that said primary alkenyl group or groups in said ester in a subsequent step is/are oxidized in the presence of an effective amount of at least one oxidizing agent, whereby an epoxide having at least one primary epoxide group is yielded.

11. A process according to Claim 10 **characterised in**, that said alcohol is esterified with said at least one alkenoic acid at a temperature of 120-280°C.

12. A process according to Claim 10 or 11 **characterised in**, that excess or otherwise unreacted alkenoic acid is removed before oxidation of said alkenyl group or groups in said ester.

13. A process according to any of the Claims 10-12 **characterised in**, that said oxidizing agent is a peroxy acid and/or a haloperoxy acid, which acid is pre-produced or produced *in situ* from an peroxide and a carboxylic acid.

14. A process according to Claim 13 **characterised in**, that said oxidizing agent is peroxyformic acid, peroxyacetic acid, peroxybenzoic acid, *m*-chloroperoxybenzoic acid, trifluoroperoxyacetic acid or a mixture thereof or therewith.

15. A process according to Claim 13 **c h a r a c t e r i s e d i n**, that said oxidizing agent is peroxyformic acid and/or peroxyacetic acid produced *in situ* from hydrogen peroxide and formic acid and/or acetic acid.

16. A process according to any of the Claims 10-15 **c h a r a c t e r i s e d i n**, that at least one acidic catalyst is present during esterification and/or oxidation.

17. A process according to Claim 16 **c h a r a c t e r i s e d i n**, that said acidic catalyst is methanesulphonic acid, *p*-toluenesulphonic acid and/or an ion exchange resin.

18. A process according to Claim 10 **c h a r a c t e r i s e d i n**, that trimethylolpropane or alkoxylated, such as ethoxylated, trimethylolpropane is esterified with Δ10,11-undecenoic acid at a temperature of 150-240°C and at a molar ratio hydroxyl to carboxyl groups of 1:0.9 to 1:1.2 and that primary alkenyl groups in yielded ester are oxidized in the presence of peroxyformic acid, peroxyacetic acid and/or *m*-chloroperoxybenzoic acid.

19. A curable composition comprising two or more components of which at least one is an epoxide according to any of the Claims 1-9.

20. A curable composition according to Claim 19 **c h a r a c t e r i s e d i n**, that said composition in addition to said epoxide comprises at least one hyperbranched or dendritic macromolecule composed of a core and at least one dendron comprising of at least one generation composed of at least one branching chain extender.

21. A curable composition according to Claim 20 **c h a r a c t e r i s e d i n**, that said core is derived from a compound having at least one reactive hydroxyl or epoxide group, that said branching chain extender is a compound having at least three reactive groups of which at least one is a carboxyl group and at least one is a hydroxyl group and that said macromolecule optionally is chain terminated and/or further functionalized.

22. A curable composition according to Claim 19 **c h a r a c t e r i s e d i n**, that said composition in addition to said epoxide comprises at least one hyperbranched or dendritic dendron comprising at least one generation composed of at least one branching chain extender.

23. A curable composition according to Claim 22 **c h a r a c t e r i s e d i n**, that said branching chain extender is a compound having at least three reactive groups of which at least one is a carboxyl group and at least one is a hydroxyl group and that said macromolecule optionally is chain terminated and/or further functionalized.

AMENDED CLAIMS

[received by the International Bureau on 3 February 2000 (03.02.00); original claims 1-23 replaced by new claims 1-27 (3 pges)]

1. A process in two or more steps for production of an epoxide having at least one primary epoxide group characterised in, that said process comprises the steps of

   i) subjecting an alcohol to esterification, at a molar ratio hydroxyl groups to carboxyl groups of 1:0.8 to 1:5, with at least one linear or branched alkenoic acid having 6-18 carbon atoms in its primary chain, one carboxyl group and at least one primary alkenyl group, whereby an esterification product having at least one primary alkenyl group is yielded, and

   ii) subjecting said at least one primary alkenyl group in said esterification product yielded in Step (i) to oxidation in the presence of an effective amount of at least one oxidizing agent, whereby an epoxide having at least one primary epoxide group is yielded.

2. A process according to Claim 1 characterised in, that the alcohol in Step (i) is a di, tri or polyalcohol or a condensation product between a di, tri or polyalcohol and at least one alkylene oxide.

3. A process according to Claim 2 characterised in, that said di, tri or polyalcohol is a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxyalkyl--1,3-propanediol, a 2-alkyl-2-hydroxyalkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)--1,3-propanediol, a 1,2,3-propanetriol or a dimer, trimer or polymer of said alcohol.

4. A process according to Claim 2 or 3 characterised in, that said di, tri or polyalcohol is neopentyl glycol, 2-ethyl-2-butyl-1,3-propanediol, glycerol, trimethylolpropan or pentaerythritol or a dimer, trimer or polymer of said alcohol.

5. A process according to Claim 2 characterised in, that said alkylene oxide is ethylene oxide, propylene oxide, butylene oxide, phenylethylene oxide or a mixture of said oxides.

6. A process according to any of the Claims 1-5 characterised in, that said alkenoic acid in Step (i) has 8-12 carbon atoms in its primary chain.

7. A process according to Claim 6 characterised in, that said alkenoic acid is Δ9,10-decenoic acid, Δ10,11-undecenoic acid or a mixture of said acids.

8. A process according to any of the Claims 1-8 characterised in, that said oxidizing agent in Step (ii) is at least one peroxy acid or haloperoxy acid.

9. A process according to Claim 8 characterised in, that said peroxy acid or said haloperoxy acid is selected from the group consisting of peroxyformic acid, peroxyacetic acid, peroxybenzoic acid, *m*-chloroperoxybenzoic acid or trifluoroperoxyacetic acid or is a mixture comprising one or more of said acids.

10. A process according to Claim 8 characterised in, that said oxidizing agent is at least one peroxy acid or haloperoxy acid produced *in situ* in Step (ii) from at least one peroxide and at least one carboxylic acid.

11. A process according to Claim 10 characterised in, that said peroxide is hydrogen peroxide and said carboxylic acid is formic acid and/or acetic acid.

12. A process according to any of the Claims 1-11 characterised in, a molar ratio hydroxyl groups to carboxyl groups in Step (i) is 1:0.8 to 1:2.

13. A process according to any of the Claims 1-12 characterised in, that said alcohol in Step (i) is subjected to esterification with said alkenoic acid at a temperature of 120-280°C, preferably 150-240°C.

14. A process according to any of the Claims 1-13 characterised in, that during Step (i) unreacted alkenoic acid is removed before oxidation in Step (ii).

15. A process according to any of the Claims 1-14 characterised in, that at least one acidic catalyst is present during esterification in Step (i) and/or oxidation in Step (ii).

16. A process according to Claim 15 characterised in, that said acidic catalyst is methanesulphonic acid, *p*-toluenesulphonic acid and/or an ion exchange resin.

17. A process according to any of the Claims 1-16 characterised in, that trimethylolpropane and/or alkoxylated trimethylolpropane in Step (i) is subjected to esterification with Δ10,11-undecenoic acid at a temperature of 150-240°C and a molar ratio hydroxyl groups to carboxyl groups of 1:0.9 to 1:1.2 and that said primary alkenyl group, in said esterification product yielded in Step (i), in Step (ii) is subjected to oxidation in the presence of peroxyformic acid, peroxyacetic acid and/or *m*-chloroperoxybenzoic acid.

18. A process according to Claim 17 characterised in, that alkoxylated trimethylolpropane is ethoxylated trimethylolpropane.

19. An epoxide having at least one primary epoxide group characterised in, that it is produced by the process according to any of the Claims 1-18.

20. A resin composition comprising two or more components of which at least one is an epoxide having at least one primary epoxide group characterised in, that said epoxide is produced by the process according to any of the Claims 1-18.

21. A resin composition according to Claim 20 characterised in, that said composition in addition to said epoxide comprises at least one hyperbranched or dendritic macromolecule comprising a core and at least one hyperbranched or dendritic dendron comprising at least one branching generation.

22. A resin composition according to Claim 21 characterised in, that said core is derived from a compound having at least one reactive hydroxyl or epoxide group.

23. A resin composition according to Claim 21 or 22 characterised in, that said dendron is composed of at least one branching chain extender derived from a compound having at least three reactive groups of which at least one is a carboxyl group and at least one is a hydroxyl group.

24. A resin composition according to any of the Claims 21-23 characterised in, that said hyperbranched or dendritic macromolecule is chain terminated and/or functionalized.

25. A resin composition according to Claim 20 characterised in, that said composition in addition to said epoxide comprises at least one hyperbranched or dendritic dendron comprising at least one branching generation.

26. A resin composition according to Claim 25 characterised in, that said hyperbranched or dendritic dendron is composed of at least one branching chain extender derived from a compound having at least three reactive groups of which at least one is a carboxyl group and at least one is a hydroxyl group.

27. A resin composition according to Claim 25 or 26 characterised in, that said dendron is chain terminated and/or functionalized.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 99/01704

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C07D 301/19, C07D 303/38, C07D 303/40, C07D 303/42 // C08G 59/14, C08G 59/20, C08G 59/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 January 2000	22-01-2000
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Eva Johansson/MN Telephone No. +46 8 782 25 00

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International application No.
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